# PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

## Process for improving Dimensional Stability of Tensilized Polyester Film

We, E. I. DU PONT DE NEMOURS AND COMPANY, a company organised and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a process for improving the thermal dimensional stability of asymmetrically, biaxially oriented (tensilized) polyester film.

Tensilized polyester film as disclosed in British Specification No. 851,875 has met with widespread acceptance, especially as a base for magnetic recording tape. It is characterized by having a very high tensile strength and a high tensile strength measured at 5% elongation, commonly known as the F—5 value. A major deficiency of such tensilized film is its tendency to shrink at elevated temperatures. A high degree of orientation, such as may be obtained by a high stretch ratio, results in high tensile properties, but this tends to increase the latent shrinkage energy. Crystallization of such films while holding under dimensional restraint, commonly achieved by heat-setting, decreases the shrinkage at elevated temperatures; this treatment, however, decreases tensile properties, notably the F—5 value; thus there is competition between the two desirable properties making it difficult to achieve the desired level of each.

According to the present invention there is provided a process for improving the thermal dimensional stability of asymmetrically biaxially oriented linear polyester film by asymmetrically biaxially orienting the film as by stretching and thereafter heat-setting at an elevated temperature characterized by heat-setting in two successive stages with the temperature in the first stage being within the range of from 50° to 250°C., and the temperature in the second stage being at least 5°C. below the temperature in the first stage, but above the second order transition temperature for the film.

The second order transition temperature is the temperature at which a discontinuity occurs in the curve of a first derivative thermodynamic quantity with temperature. It is correlated with yield temperature and polymer fluidity and can be observed from a plot of density, specific volume, specific heat, sonic modulus or index of refraction against temperature.

In its preferred form the present invention is adapted to the process of stretching according to British Specification No. 890,004 which in its general terms involves heating a substantially amorphous film to a temperature of 80°C. to 90°C., stretching the film at 80°C. to 90°C. to at least 3.3 times its initial width, and heating the film to a temperature of 90°C. to 160°C., and stretching at a temperature of 90°C. to 160°C. to 3.0 to 6.0 times its initial length. Such film is normally heat-set by passing a pair of heated nip rolls at a temperature above that of the second direction stretch and between 135°C. and 250°C.

According to the present invention heat-setting is by a two-stage process, where the first stage is according to the process of British Specification No. 890,004 employing a pair of heat-setting rolls immediately following the fast rolls of the last stretching step with the second stage at a temperature lower than the first by at least 5°C., preferably 10°C., employing a second pair of heat-setting rolls. The particular advantage of the present invention is in enabling the production of a tensilized film having a high tensile strength at 5% elongation without substantially sacrificing thermal dimensional stability.

The minimum temperature difference between the first and second heat-setting stage of the present invention is 5°C., with at least

10°C. being preferred. The operable maximum temperature difference is a function of the maximum operable temperature of the first stage and the minimum operable temperature of the second stage. The first stage heat-set is accomplished in the range of 150°C. to 250°C. the maximum temperature being approximately 5° to 10°C. below the melting point for polyethylene terephthalate film and for copolyesters of ethylene terephthalate, containing isophthalic or other dibasic acids. The final heat-setting is accomplished at a temperature above the second order transition temperature. This final heat-setting temperature varies with the molecular weight of a polymer, and with the nature of the polyester, i.e. polyethylene terephthalate or its copolyesters; for polyethylene terephthalate the minimum temperature has been found to be about 80°C. Temperatures below 80°C. result in poor quality film from the standpoint of wrinkles, especially where it is desired to impart a small degree of relaxation in the latter stage.

The following examples will serve to further illustrate the principles and practice of this invention.

EXAMPLE 1.

Forty separate samples of tensilized polyethylene terephthalate film of a nominal thickness of 0.001 inch were produced by the method of U.K. Specification No. 890,004 except that heat-setting was accomplished in two stages. Of these 40 samples, 24 were heat-set in a sequence (called "upstage") in which the first pair of heat-set rolls was at a lower temperature than the second pair. Sixteen were heat-set by the so-called "downstage" sequence characterizing this invention, in which the first pair of heat-set rolls was at a higher temperature than the second pair. Table I indicates the temperatures employed; the fast rolls indicated are the second pair of nip rolls which draw the film in the second direction according to the cited patent. HS—1 and HS—2 are the first and second pairs of heat-setting rolls through which the film passes in this two-stage heat-setting process. TDX is the stretch ratio in the transverse (at right angles to the direction of extrusion) direction, LDX is the stretch ratio in the longitudinal or extrusion direction. Average values of dimensional stability (expressed as % shrinkage) and F—5 values are given.

TABLE I

| | Heat Setting Sequence | |
|---|---|---|
| | Upstage | Downstage |
| TDX | 3.4 | 3.4 |
| LDX | 4.67 | 4.67 |
| Fast Roll Temp. °C. | 151 | 152 |
| HS—1 Roll Temp. °C. | 155 | 180 |
| HS—2 Roll Temp. °C. | 190 | 150 |
| Dim. Stab. at 105°C. | | |
| % LD Shrinkage | 2.65 | 1.77 |
| % TD Shrinkage | 1.22 | 1.06 |
| $F_5$, psi | 23,400 | 22,200 |

A sample of film produced according to U.K. Specification No. 890,004 had an LD dimensional stability of 3.1% shrinkage at 105°C. and an F—5 of 20,000 psi.

EXAMPLE 2.

A number of rolls of polyethylene terephthalate film were stretched and heat-set as in Example 1, with samples made and compared among the various thicknesses of tensilized film. The fast roll temperature was 150°C., the first pair of heat-set rolls was at 150°C., and the second pair of heat-set rolls was at 200°C. in the "upstage" sequence. In the "downstage" sequence, the fast rolls were at 150°C., the first pair of heat-set rolls was at 195°C., and the second pair of heat-set rolls was at 175°C. The average percent LD shrinkage and F—5 values are set forth in the following table:

TABLE II

| Nominal Thickness of Finished Film, Inches | Heat-Setting (Number of Samples) | Dimens. Stability (% LD Shrinkage at 105°C.) | F—5 (psi) |
|---|---|---|---|
| 0.0005 | Upstage (149) | 3.14 | 23,500 |
| | Downstage (104) | 1.79 | 22,200 |
| 0.001 | Upstage (134) | 3.10 | 25,300 |
| | Downstage (233) | 1.93 | 22,400 |
| 0.0015 | Upstage (6) | 2.96 | 25,500 |
| | Downstage (38) | 1.69 | 22,900 |

EXAMPLE 3.

A number of runs were made as in Example 2, but with 3% longitudinal relaxation (i.e. shrinkage) permitted between the LD fast rolls and the quench rolls following heat-setting. The results are summarized in Table III.

TABLE III

| Heat-Setting Sequence | HS—1 °C. | HS—2 °C. | Dimens. Stability (% LD Shrinkage at 105°C.) | F—5 (psi) |
|---|---|---|---|---|
| Upstage | 155 | 180 | 2.96 | 24,200 |
| Upstage | 170 | 180 | 2.53 | 22,300 |
| Equal | 180 | 180 | 1.94 | 21,400 |
| Downstage | 190 | 184 | 1.77 | 20,400 |
| Downstage | 190 | 170 | 1.70 | 20,600 |
| Downstage | 185 | 150 | 1.06 | 20,600 |

EXAMPLE 4

Separate rolls of tensilized film as in Example 2 were made with a lower range of temperature for the final heat-set roll. Conditions were as follows:

| | |
|---|---|
| LD slow roll: | 134°C. (Note 1) |
| LD fast roll | 140°C. (Note 2) |
| First heat-set rolls: | 195°C. (Note 3) |
| Second heat-set rolls: | As indicated in Table IV |
| Quench rolls: | 27°C. |
| LD stretch ratio: | 4.64 (Note 4) |
| Relaxation pattern 0,0 | 1.1 (Note 5) |
| Film speed: | 63 yards per minute. |

Notes:

1. This is the effective LD stretching temperature.
2. This pair of rolls effects some heat-setting action, although the primary function is to advance the film at a speed several times that of the slow rolls (this determines the stretch ratio).
3. The film at this speed (63 yards/minute) and for operable ranges of thickness (5 mils or less) is found to attain a temperature within 1°C. of the temperature

of the heated rolls; under the most adverse conditions it is not more than 2° to 5°C. below the temperature of the roll. The significant feature is the difference in temperatures of successive rolls; the profile of temperatures attained by the film parallels the profile of roll temperatures.

4. This is the ratio of the speed of the film entering the slow rolls.
5. The relaxation pattern 0, 0, 1.1 indicates no relaxation between the fast rolls and first heat-set, none between the first and second heat-set, and 1.1% between the second heat-set and quench.

TABLE IV

| Film Roll Number | Second Heat-Set, °C, | F—5 (psi) | Dimensional Stability (% Shrinkage at 105°C.) | |
|---|---|---|---|---|
| | | | LD | TD |
| 1 | 140 | 24,000 | 1.33 | 0.66 |
| 2 | 140 | 23,200 | 1.39 | 0.81 |
| 3 | 130 | 22,900 | 1.32 | 0.75 |
| 4 | 130 | 23,300 | 1.48 | 1.06 |
| 5 | 120 | 23,200 | 1.37 | 1.17 |
| 6 | 120 | 23,000 | 1.56 | 1.01 |
| 7 | 110 | 24,700 | 1.58 | 0.91 |
| 8 | 110 | 23,700 | 1.78 | 1.06 |
| 9 | 100 | 35,200 | 1.74 | 1.06 |
| 10 | 100 | 24,200 | 1.80 | 1.12 |

EXAMPLE 5.

A series of rolls of film similar to those of Example 4 was produced to extend the test below 100°C. Conditions were the same except that the LD stretch ratio was 4.57. This slightly lower LD stretch ratio results in lower LD tensile properties and less shrinkage at elevated temperatures.

| Film Roll Number | Second Heat-Set, °C. | F—5 (psi) | Dimensional Stability (% Shrinkage at 105°C.) | |
|---|---|---|---|---|
| | | | LD | TD |
| 1 | 140 | 23,100 | 1.16 | 0.75 |
| 2 | 140 | 23,700 | 1.18 | 0.67 |
| 3 | 80 | 24,100 | 1.70 | 1.12 |
| 4 | 80 | 24,200 | 1.53 | 1.05 |

Although the present invention is exemplified herein as applicable to polyethylene terephthalate film, it is equally applicable to linear copolyesters of ethylene terephthalate and other dibasic organic acids, for example isophthalic.

WHAT WE CLAIM IS:—

1. A process for improving the thermal dimensional stability of asymmetrically biaxially oriented linear polyester film by asymmetrically biaxially orienting the film as by stretching and thereafter heat-setting at an elevated temperature *characterized by* heat-setting in two successive stages with the temperature in the first stage being within the range of from 150° to 250°C., and the temperature in the second stage being at least 5°C. below the temperature in the first stage, but above the second order transition temperature for the film.

2. A process according to Claim 1 characterized in that the temperature in the second stage is at least 10°C. below the temperature in the first stage.

3. A process according to Claim 1 for asymmetrically biaxially orienting linear polyester film substantially as hereinbefore described with reference to any one of the Examples.

4. Polyester film when proluced by the process of any one of Claims 1 to 3.

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